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Sulfonated poly(arylene ether ketone) membranes bearing proton conducting cross-linker for fuel cell application

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In polymer electrolyte membrane fuel cells, the proton conductivity of sulfonated membrane materials rely on loaded sulfonic acid groups, which absorb water and act as proton exchange sites that facilitate the proton conduction. These membranes usually exhibit an increasing conductivity with increasing degree of sulfonation (DS) in the fully hydrated state. However, the mechanical properties of sulfonated membranes tend to deteriorate progressively upon acid loading *via* excess water uptake. Moreover, a high water uptake may be accompanied by a high methanol permeability.

Cross-linking is a simple and efficient way to suppress this excess water uptake and enhance the mechanical strength. Many cross-linked membranes have been considered using different cross-linking methods [1-10].

In hopes of boosting the proton conductivity of the sulfonated polymers, in this work, an easy process is presented for making a cross-linked proton exchange membrane with a high proton conductivity. First, functional sulfonated poly(arylene ether ketone) (SPAEK) with a defined structure was produced using the direct synthesis method. The direct synthesis of sulfonated polymers has many advantages, such as an excellent stability and a well defined DS and chain structure. This method can be used to prepare cross-linked membranes without sacrificing the sulfonic acid groups. The free carboxylic group was activated with N-hydroxysuccinimide and then reacted with disulfonic acid-benzidine diamines, a functional cross-linking reagent containing both sulfonic acid group and amine group, to prepare a series of cross-linked SPAEK (CSPAEK) membranes. Cross-linked membranes can withstand higher operating temperatures so that contaminants, such as carbon monoxide, poison the platinum catalyst as little as possible. Using a chemically cross-linked system, polymer electrolyte membranes could be produced with a high conductivity and excellent mechanical strength. The effects of the cross-linking density on the physical, chemical and electrochemical properties of the membranes were investigated.

The cross-linking hindered the mobility of the polymer chains and thus strongly affected the water uptake and the methanol permeability of the membranes. Also, as the cross-linker used in this study bore sulfonic acid groups, cross-linking did not lead to a noticeable loss of the proton conductivity. The cross-linked SPAEK membrane with 20% cross-linking density, CSPAEK-20% membrane, exhibited a high proton conductivity of 0.045 S cm^{-1} associated with a high IEC value of 1.78 mmol g^{-1} but a low methanol permeability of 4.3×10^{-7} cm^2 s^{-1}. The CSPAEK-20% membrane also showed excellent cell performance and oxidation resistance.

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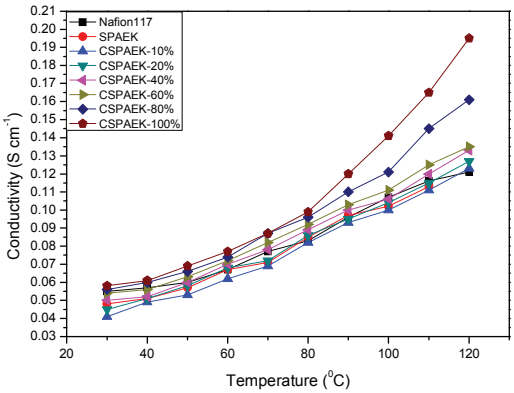

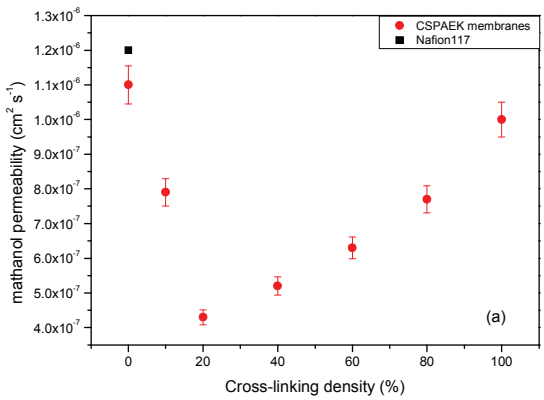

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